SURVEY OF CONTAMINANTS IN SEDIMENT AND BIOTA WITHIN THE GRASSY ISLAND CONFINED DISPOSAL FACILITY, WYANDOTTE NATIONAL WILDLIFE REFUGE

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Background

Wyandotte National Wildlife Refuge is located in the Detroit River and consists of two small islands, Grassy and Mamajuda, and the surrounding waters out to approximately the six-foot depth contour. The refuge was established in 1960 primarily to protect the shallow water areas and associated submerged vegetation and benthic invertebrates historically utilized by diving ducks in the fall and winter. The refuge is administered by the Shiawassee NWR and managed as wilderness.

Since the early 1960s, Grassy Island has served the U.S. Army, Corps of Engineers as a final receptacle for polluted dredged sediments from Lake St. Clair and the Detroit River, including the Trenton Channel. The island was converted into an 80-acre confined disposal facility (CDF) in 1960 consisting of two cells surrounded by dikes. Dredged material was hydraulically pumped as a slurry into the receiving cells and allowed to settle. The resulting water was discharged back into the river via an overflow weir.

This CDF preceded Public Law 91-611 (1970) which initiated the Great Lakes-wide CDF program. Therefore, this CDF lacks the confinement technology employed in later CDF designs. Specifically, the CDF was constructed without liners and caps, and with dikes composed of sand and clay without riprap revetment protection. Subsequent to the original design, the dikes were raised in the 1960's and the capacity further expanded in 1971. In 1985-86, the dikes adjacent to the navigation channel were repaired and reinforced with filter cloth and riprap revetment to prevent failure of the structure due to riverine and navigational forces. Both cells currently remain uncapped resulting in polluted sediments being exposed over much of the CDF.

Since the mid-1980's, little of the 1.9 million cubic yard design capacity remains available for additional dredged sediment disposal. Each cell retains a small open water pond that is attractive to waterfowl. The majority of the CDF supports a mixture of emergent, scrub-shrub and forested wetland types, also attractive to a variety of wildlife. In a 1987 survey of nine CDFs throughout the Great Lakes, soils within the vegetated portions of the Grassy Island CDF had some of the highest levels of mercury and other heavy metals (Beyer and Stafford, in press). Earthworms associated with this soil showed positive bioaccumulation of several of the heavy metals. The CDF dikes also have attracted a small breeding colony of common terns (*Sterna hirundo*).

As a result of the attractive wildlife habitat to develop within the facility, the East Lansing Field Office undertook the task of identifying and quantifying contaminants in aquatic sediments in the two small ponds, and quantifying contaminant residues in birds utilizing all habitats on the island. Aside from results on the common tern colony, this study does not evaluate wildlife usage of and risk from the shallow water areas outside the CDF that may be affected by inplace sediment pollution and CDF leakage.

Methods

A survey of the sediment and biota of the Grassy Island CDF was conducted during the 1988 field season. Biota collections centered on adult and juvenile waterfowl from the ponds, woodcock (*Philhela minor*) from the terrestrial wetlands, and eggs from the common tern colony on the island and from comparison colonies both upriver and downriver of the site.

A single composite sediment sample was collected in June from each of the ponds within the north and south cells of the CDF. All waterfowl and woodcock were collected in June from within the CDF with firearms using steel shot. Each bird was weighed whole prior to preparing the liver and skinless breast muscle for chemical analysis. Woodcock wings were also submitted for chemical analysis. All eggs were individually homogenized. Equal aliquots were taken from each egg and combined to form a single composite sample for each breeding colony.

A conversion factor was calculated for each individual egg as a ratio of the mass of the actual egg contents to the mass of the maximum egg contents, as determined by water displacement. A mean of the individual conversion factors for the eggs from a breeding colony was used to represent the composite egg sample. This conversion factor was used to express egg contaminant residues on a fresh wet weight basis, *i.e.* at the time the eggs were laid.

Both sediment samples were subjected to analyses for organochlorine pesticides including total PCBs (gas-liquid chromatography), aliphatic and polycyclic aromatic hydrocarbons (gas chromatography/mass spectrometry (GC/MS) with selective ion monitoring), heavy metals (sequential inductively coupled plasma emission spectrometry), and mercury (cold vapor atomic absorption). When sample mass was sufficient, all biota were analyzed for organochlorine pesticides, aliphatic hydrocarbons, heavy metals, mercury and percent lipid. Percent moisture was determined for all samples. All analyses were conducted by contract laboratories to the Patuxent Analytical Control Facility (PACF).

Quality Assurance/Quality Control (QA/QC) of the contract laboratories was monitored by the PACF through analysis of duplicate samples, matrix and reagent blanks, spiked samples, calibration checks, standard reference material samples, method blanks and GC/MS confirmation. Based on the QA/QC program, PACF determined that the results of the analyses were acceptable (Appendix 1).

The two sediment samples and the colonial waterbird egg composites were submitted for the H-4-II E rat hepatoma bioassay to measure enzyme induction potencies of sample extracts expressed in units of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) equivalents. The bioassay was conducted by the Pesticide Research Center, Department of Fisheries and Wildlife, Michigan State University (Appendix 2).

Results and Discussion

Sediment

Soils and sediments within the CDF have elevated concentrations of a variety of organic and inorganic compounds (Tables 1 and 2). These data support the original need to confine these sediments when compared to the various jurisdictional criteria established as guidelines for open water disposal of dredged sediments. This sediment/soil contamination is greatly elevated over what is considered to represent background levels for heavy metals and total PCBs in Lakes St.Clair and Erie sediments (International Joint Commission 1982). These values from the CDF also fall well within the range of individual instream Detroit River sediment values quantified since 1980 for heavy metals and total PCBs, as summarized in the Stage 1 Remedial Action Plan of 1991 for the Detroit River Area of Concern. Specifically, these values are comparable to or exceed the maximum median values for these compounds in thirty sections of the river (3 lateral sections by 10, 3-mile longitudinal reaches).

The results also show elevated levels of individual Polycyclic Aromatic Hydrocarbon (PAH) and organochlorine compounds compared to soil cleanup criteria developed by the Michigan Department of Natural Resources under the authority of the Michigan Environmental Response Act, Public Act 307 of 1982, as amended. Chlordane, DDE, DDD, phenanthrene and benzo(g,h,i)perylene exceed the soil criteria established to protect ground water. Chlordane, PCBs and 8 PAH compounds exceed the soil criteria protective for exposure by direct contact. At this time, only a limited number of soil criteria have been developed for the protection of surface waters, nor have the individual aliphatic hydrocarbon compounds detected in this study been evaluated. Only PCBs and chlordane exceed the soil cleanup criteria protective of surface waters.

In general, soil-borne contaminants within the CDF, as quantified by Beyer and Stafford (in press), are comparable or lower than contaminants in the pond sediments. The continual sorting of the confined material with each new input of dredged slurry may have resulted in the finer and more contaminated sediments being ultimately deposited near the overflow weirs. These areas now constitute the ponds within the two cells. In addition, the gradual incorporation of organic plant matter into the soils as the terrestrial vegetation developed within the CDF, may have helped "dilute" the contaminants in these soils. Other processes, such as leaching and erosive forces also may have contributed to the observed pattern. The one exception to this pattern is the high levels of total PAHs in the soils relative to the sediments.

Of considerable note are the high levels of bioassay-derived dioxin equivalents found in the pond sediments. These levels are unexpectedly high compared to the levels of total PCBs and PAHs; classes of compounds which are known to induce the bioassay response. Although the Aliphatic Hydrocarbons are elevated in the CDF sediments, these compounds are not known to elicit a similar response. Work within the Fox River basin in Wisconsin (Fabacher *et al.* 1991) has shown considerable carcinogenic and non-carcinogenic responses by medaka (*Oryzias latipes*) to alkyl-substituted PAHs in sediment. This class of petroleum and other fossil fuel compounds typically result from non-combustion sources. Dibenzothiophenes (sulfur substituted analogs to polychlorinated dibenzofurans) were similarly implicated. Neither of these two classes of compounds were analyzed in this present study and may account for the elevated bioassay results. In addition, various PAHs are known carcinogens.

The origin of the elevated bioassay response should be evaluated further by reanalyzing the CDF soils and sediments with the bioassay procedure via fractionated extracts. This would more accurately identify the specific extract(s) contributing the bulk of the induction response. This information will be useful in assessing risks to wildlife, since various compounds differentially bioaccumulate in biota through trophic levels. The remedial actions ultimately to be taken by the Service at this facility would likely be more thorough if the bulk of the bioassay response was a result of total PCBs or similar compounds which readily bioaccumulate through the food chain.

Waterfowl

Residues of organic contaminants were detected in approximately half of the skinless breast muscle and liver samples (Tables 3 and 4). In individual birds, the concentration of the detected compounds in muscle and liver were similar to one another, as was noted in previous studies (Kim *et al.* 1984, 1985, Sarkka *et al.* 1978). Owing to the low lipid content of both types of specimens (0.6-2.5% for muscle and 1.3-5.4% for liver), when total PCBs were detected, the lipid weight concentrations readily exceeded the USFDA Tolerance Level for poultry in interstate commerce (3.0 ug/g, lipid weight; 21 CFR 109.30). The removal of the skin and associated subcutaneous fat from the muscle samples, resulted in the low lipid values. Only three of 14 samples with detectable DDT compounds exceeded the Tolerance Level for DDT and metabolites (5.0 ug/g, lipid weight).

As was demonstrated in 1985 within the south cell of the Saginaw Bay CDF (USFWS unpublished data), as little as ten days of exposure is required for gamefarm mallard hens (*Anas platyrhynchos*) to exceed the Tolerance Level for total PCBs. Over the 86-day exposure period, the mean body burden for both PCBs and p,p'-DDE continued to increase and only total PCBs began to level off by day 86. This rapid bioaccumulation occurred in the presence of relatively low levels of PCBs in the sediments of the CDF. Only two of nine sediment samples had detectable PCBs (0.49 and 0.71 ug/g, wet weight). The marginally higher levels of PCBs in the Grassy Island sediments (1.0 and 1.1 ug/g, wet weight) suggest that bioaccumulation of PCBs and DDE by waterfowl should be similarly rapid. Foley and Batcheller (1988) found significant over winter bioaccumulation of total PCBs, DDT and metabolites, and other organochlorine pesticides by waterfowl in the Niagara River, New York.

There is a remarkable similarity in wet weight concentrations of organic residues in livers between juvenile and adult waterfowl. There was insufficient mass of breast muscle in juvenile waterfowl to make a similar comparison. Generally, the Canada geese (*Branta canadensis*) exhibited lower concentrations of organic compounds than the dabbling ducks. The proportion of plant and animal matter in the diet of various waterfowl species appears to be important in determining body burdens (Smith *et al.* 1985, Llorente *et al.* 1987).

The levels of PCBs and DDT in breast muscle and liver tissues are comparable to levels found in wintering waterfowl of the same species in the Niagara and Hudson Rivers, New York (Kim *et al.* 1984, 1985). Like the Detroit River, these two river systems have a history of water quality problems, including the presence of organochlorine compounds. In the Detroit River, our results are considerably lower than data collected by Smith *et al.* (1985) on wintering waterfowl in the vicinity of Mud Island, an island in the vicinity of the CDF. Two factors may account for these elevated levels. First, the species collected were wintering diving ducks which feed at a higher trophic level than the geese and dabbling ducks collected in our study. Secondly, the analysis of the diving ducks by Smith and coworkers were conducted on "roaster-ready" carcasses, which included the skin and associated subcutaneous fat. As one might expect, the lipid content of the carcasses of the three species of wintering waterfowl was considerably higher (means of 16.3, 17.8 and 20.7 %) than the CDF waterfowl samples (0.6-2.5% for muscle, 1.3-5.4% for liver). Organochlorine compounds are lipophilic and are readily accumulated in these fatty tissues. Therefore, when the wintering waterfowl data are expressed on a lipid weight basis (37-67 ug/g for PCBs, 2.9-9.1 ug/g for DDT), the results are similar to our study results. In addition, sediments collected in the vicinity of Mud Island (Smith *et al.* 1985) contained levels of PCBs (0.67 ug/g, wet weight) and DDT (0.05 ug/g, wet weight) similar to the CDF pond sediments.

Lead was the only heavy metal to be detected at levels of concern (Tables 5 and 6). Two liver samples possessed greater than 2.0 ug/g, fresh weight, the level considered as elevated (as reviewed in Eisler 1988). In the American kestrel (*Falco sparverius*), greater than 2.0 ug/g of lead in the liver was associated with suppressed growth rates (Hoffman *et al.* 1985).

Residues of mercury were detected at levels well below those found in waterfowl from northwestern Ontario and Lake Paijanne in Finland (Vermeer and Armstrong 1972, Vermeer *et al.* 1973, Fimreite 1973, 1974, Sarkka *et al.* 1978). These areas have a history of water quality problems related, in part, to improper disposal of mercury from pulp and paper mills or chlor-alkali plants. In the present study, the levels of mercury detected in adult breast muscle averaged 37 percent of that in the liver, and was similar to the mean value (32%) reported from northwestern Ontario (Fimreite *et al.* 1971). While our results are lower than the above cited studies, the liver values are comparable to waterfowl collected from the Ottawa River in the vicinity of a pulp and paper mill where mercury contamination was suspected (Fimreite 1974).

The relatively low levels of mercury in the CDF waterfowl samples are unexpected, given the historical mercury problems in the St. Clair-Detroit River system, and the high levels detected in soils and earthworms within the CDF (Beyer and Stafford, in press). The results were similar to the results from waterfowl surveys over broad geographical areas in Canada (Vermeer and Armstrong 1972, Pearce *et al.* 1976). Higher residues of mercury were expected in the CDF waterfowl based on herring gull (*Larus argentatus*) data from the Detroit River and western basin of Lake Erie (Struger *et el.* 1987). Except for the two blue-winged teal (*A. discors)*, the waterfowl liver samples had less than half the mercury concentration of herring gull livers from a colony in Lake Erie, which had mercury residues in eggs that were seven times lower than eggs from a gull colony in the Detroit River near the CDF. Despite the higher trophic position of the herring gull, the CDF waterfowl were expected to have higher mercury residues than those detected. Only one sample, the liver from the drake blue-winged teal, exceeded 2.0 ug/g mercury, fresh weight, the level associated with reproductive and behavioral deficiencies in domestic mallards (as reviewed in Eisler 1987).

Woodcock

Only one woodcock was collected from the CDF, although several were flushed while traversing the dikes. Due to the small sample masses derived from this single specimen, only organic contaminants were quantified. The residues of organic compounds in the liver and the skinless breast muscle are similar to those quantified for waterfowl (Tables 3 and 4). Although the soils and sediments within the CDF have similar levels of these compounds, the foraging habitat for woodcock and waterfowl are different. While the woodcock forage in moist terrestrial and wetland habitats, the ducks predominantly forage in the ponds. The dense stands of reed (*Phagmites australis*) that characterize much of the terrestrial wetlands in the CDF, and where the woodcock was collected, would not be very attractive to foraging waterfowl. Despite these differences, the common link is their reliance on an invertebrate prey base derived from soils and sediments with similar contaminant loads. This may help explain the similarity between woodcock and waterfowl body burdens.

As was the case for waterfowl, the lipid weight conversion for total PCBs in the skinless breast muscle exceeds the USFDA Tolerance Level for poultry. Due to the presence of subcutaneous fat, it is reasonable to assume that a skin-on breast muscle sample would be further elevated. The liver sample was too small to permit a percent lipid determination. However, lipid weight concentrations of these organic compounds in the liver would be expected to fall within the range of values found in waterfowl.

The highest organochlorine concentrations were found in the wings (footnotes to Tables 3 and 4). These data can be compared to Michigan data from national woodcock wing surveys undertaken during the early to mid-1970s which reported values on a lipid weight basis for five, 25-wing composites (McLane *et al.* 1973, 1978, 1984). Since the wing sample from the CDF was of insufficient size to permit determination of lipid content, and the previous surveys failed to report lipid content of the wings, we assumed that the lipid content in woodcock wings would be similar to mallard wings (14.4%), for which Michigan data are available (Prouty and Bunck 1986).

The lipid weight approximations of organic residues in the woodcock wing from the CDF are presented in Table 7 and compared to the range of composite values from the three previous surveys. For all detected compounds except p,p'-DDE, concentrations in the wing from the CDF exceed the maximum composite values from the later two surveys. In the case of total PCBs, the woodcock wing from the CDF is almost five times higher than the maximum composite value from any of the surveys. For DDE, the wing falls within the range of composite values. Compared to the mallard wing data for Michigan (Prouty and Bunck 1986), the woodcock wings greatly exceed the maximum mallard wings for both total PCBs and DDE.

Although the locations of the 125 individual woodcock comprising the composites for each survey year are not reported by McLane *et al.* (1973, 1978, 1984), it is not likely that the birds were collected from sites with as obvious a potential wildlife risk as the CDF. It also should be noted that there would likely be individual wings within the composites with residues comparable to the wings from the CDF. Considering the general declining residue trend in adult woodcock wings during the first half decade of the 1970s, the relatively high levels of most of the detected compounds in the bird from the CDF suggest that the site does pose a hazard to woodcock, and ultimately to higher trophic level predators.

Colonial Waterbirds

Prior to our planned collection of common tern eggs from the CDF, the colony was abandoned and all eggs were either destroyed or removed. Therefore, site specific residue data for this colony is unavailable. However, eggs were collected from a common tern colony less than 15 miles downriver of the CDF, a Forster's tern (*S. forsteri*) colony in Lake St. Clair, and two common tern colonies from the Saginaw River and Bay. The Saginaw Bay colony is similarly located on the dikes of a CDF. All four colonies are situated in or immediately downriver of three Areas of Concern designated by the International Joint Commission due to historical water quality degradation and beneficial use impairment. Therefore, these colonies should provide estimates of the level of contamination to expect in common tern eggs from the Grassy Island CDF.

The results show elevated levels of total PCBs, dioxin-equivalents and mercury in the four egg composites (Tables 8 and 9). The results for PCBs greatly exceed the USFDA Tolerance Level for eggs in interstate commerce (0.3 ug/g, wet weight; 21 CFR 109.30). Total PCBs in the four egg composites were remarkably similar to one another, and to previous sampling efforts at tern colonies in Saginaw Bay and Green Bay (Hoffman *et al.* in prep.) and Lake Ontario (Weseloh *et al.* 1989). The composites were also higher than eggs collected in previous studies from sites used for control purposes within the Great Lakes basin (Hoffman *et al.* in prep., Kubiak *et al.* 1989, Niemi *et al.* 1986, Weseloh *et al.* 1989). In the Detroit

River, Weseloh and co-workers (1989) quantified total PCBs of 8.24 ug/g, wet weight in common tern eggs collected in 1981 from Fighting Island, an island adjacent to Grassy Island on the Canadian side of the river. The four egg composites had approximately half the total PCB concentrations that were detected in common and Forster's tern eggs collected in 1982 and 1983 from the mouth of the Fox River in Lower Green Bay (Kubiak *et al.* 1989, Smith *et al.* 1990). The Fox River is the largest known point source of PCBs and dioxin-like compounds to the Great Lakes. Therefore, it is reasonable to expect the common tern eggs from the CDF to have total PCB residues in the range of 7-11 ug/g, fresh weight; the levels detected for the four comparison colonies. This expectation is supported by longterm monitoring data which indicates that herring gull eggs from Fighting Island have among the highest total PCBs levels found in the Great Lakes (Struger *et al.* 1985).

PCB concentrations in this range would be expected to result in reproductive failure in the common tern colony. The lowest observable effect level for total PCBs in studies of avian reproduction (chickens) is 0.87 ug/g (Britton and Huston 1973), while 5-15 ug/g clearly impairs the hatchability of chicken eggs (as reviewed in Kubiak *et al.* 1989). In a 1983 study of Forster's tern in Green Bay (Kubiak *et al.* 1989), reproductive success was impaired at median egg concentrations of 22.2 ug/g of total PCBs, among other contaminants. Not only were PCBs (specifically aryl hydrocarbon hydroxylase(AHH)-active PCB congeners) an intrinsic factor to poor hatchability, but extrinsic factors (parental attentiveness) contributed to the poor reproductive outcome. In a companion study by Hoffman *et al.* (1987), Forster's tern hatchlings from Green Bay had elevated microsomal AHH activities, shorter femur lengths, higher ratios of liver to body weight and a higher frequency of developmental abnormalities than hatchlings from a control colony. Common tern embryos and hatchlings from Saginaw and Green Bay colonies in 1984 and 1985 exhibited similar reproductive impairment with reduced femur length to body weight ratios, and elevated hepatic microsomal AHH activities (Hoffman *et al.* in prep.) Both measures of embryonic health were inversely related to total PCB residues in the eggs. The egg residues are similar to those quantified in egg composites in the present study. For the bald eagle (*Haliaeetus leucocephalus*), total PCBs of greater than 4-6 ug/g, fresh weight in addled eggs, were associated with measures of productivity below normal levels (Best *et al.* 1990, Wiemeyer *et al.* 1984, Wiemeyer 1990). The effects of PCBs on avian embryos may be exacerbated by dieldrin, similar to the additive effects of these two compounds on adult survival in pheasants (Dahlgren *et al.* 1972).

As might be expected from the PCB results, the H-4-II E bioassay of three of the egg composites yielded elevated results. The bioassay-derived dioxin equivalents for these eggs were similar to previous results for common tern eggs composites in 1986 from both Saginaw Bay and northern Lake Huron (Tillitt *et al.* 1991). While no criteria have yet been developed for avian reproduction in terms of bioassay-derived dioxin equivalents, effects can be estimated from egg injection studies using actual 2,3,7,8-TCDD. The no observable adverse effect level for white leghorn chicken embryos injected with 2,3,7,8-TCDD, is 20 pg/g in the egg contents (Verret 1976). At the other extreme, 1,000 pg/g of 2,3,7,8-TCDD injected into chicken eggs, completely inhibits hatching of chicks (Higginbotham *et al.* 1968). If one assumes that the Grassy Island CDF eggs would have had bioassay-derived equivalents similar to the analyzed samples (likely from the above discussion on total PCBs), then it would be expected that the common terns nesting on the CDF would experience some degree of egg-intrinsic reproductive impairment.

Since small forage fish dominate the diet of common terns and were not observed in either of the CDF ponds, the bulk of the PCBs and dioxin equivalents should be considered as derived from the river and sediments, and not from the CDF. Since the refuge includes the shallow water shoals surrounding the CDF, the refuge as a whole should be considered, in part, a source of this contamination. Data from Hamilton Harbor (Gilbertson 1974), an Area of Concern in Lake Ontario, suggest that while common terns may arrive on the breeding grounds with measurable levels of PCBs, levels of organochlorine compounds and PCBs greatly increase with time on the breeding grounds. It was concluded that the source of the contamination to eggs and adult breast tissues was of local origin. Therefore, it is reasonable to assume that the common terns arrive at the CDF with relatively low body burdens and would accumulate the estimated levels of PCBs and dioxin equivalents in the vicinity of Grassy Island.

Mercury is the most problematic of the detected heavy metals in the egg composites. The mercury residues are over four times greater than the mean levels detected in herring gull eggs collected on Fighting Island in 1981-82 (Struger *et al.* 1985). More importantly, the residues fall within the range of 0.79-2.0 ug/g associated with impaired reproduction in various bird species (as reviewed in Eisler 1987). In feeding experiments, adverse reproductive effects were noted at 0.85 ug/g mercury in mallard eggs (Heinz 1979), and 0.5-1.5 ug/g in ringed-necked pheasant (*Phasianus colchicus*) eggs (Fimreite 1971).

For fish eating birds, Eisler (1987) cites mercury residues in eggs of 1.3-2.0 ug/g, fresh weight associated with reduced hatching success in the white-tailed sea-eagle (*H. albicilla*) and the common loon (*Gavia immer*). For the common tern, Fimreite (1974) noted reduced hatching and fledgling success at mercury levels in eggs within the range of 1.0-3.6 ug/g, wet weight. Similarly, Conners *et al.* (1975) reported poor reproductive success at a common tern colony in Hamilton harbor associated with egg residues of 1.1 ug/g mercury, wet weight. However, this study concluded that mercury and other detected metals did not appear to be the primary cause of the reproductive failure.

Barr (1986) suggests that mercury may have impaired loon reproduction in northwestern Ontario through reduced egg production and aberrant adult behavior related to nest and territory fidelity, rather than through embryotoxic effects. In feeding studies with chickens, Scott *et al.* (1975) observed significant reductions in adult production of eggs, as well as egg hatchability resulting from methylmercury. However, these effects were noted at total mercury concentrations in the egg several times greater than the levels cited by Barr (1986). Methylmercury is not known to be teratogenic, but causes neurologic injury in both adults and developing embryos (Peereboom-Stegeman 1987). Therefore, in the case of the common loon, the effects of mercury on adult behavior and egg production may be manifested at lower exposure levels than embryotoxic effects. The above studies suggest that the terns and the common loon may have a similar sensitivity to mercury. Mercury residues in the egg composites are of a magnitude of concern for the reproductive health of the common tern colony at the CDF.

The residues of other compounds detected in the egg composites appear to be less of a concern to the health of the common tern colony. For example, Ridgeway and Karnofsky (1952) estimated the LD_{50} for elemental copper in 4-day old white leghorn chicken embryos to be 0.6 mg/egg, for a 50-60 g egg. Expressed in a form applicable to any size egg, this represents a LD_{50} concentration of 10-12 ug/g, wet weight of copper. The lowest or no observable adverse effect level would be considerably lower than this value, and likely exceed the 0.69-0.81 ug/g of copper detected in the tern egg composites.

The detected levels of p,p'-DDE are low compared to sites within the Great Lakes which are believed to be relatively unpolluted (Kubiak *et al.* 1989, Niemi *et al.* 1986, Weseloh *et al.* 1989). Data presented by Fox (1976) suggest that mean egg residues of 3.42 ug/g, wet weight of DDE resulted in abnormalities in shell structure and composition which led to embryo death and reproductive impairment in a colony of common terns in Alberta. This level was nearly half the DDE concentration (6.77 ug/g, wet weight) associated with shell thinning and embryo loss due to shell denting and crushing.

Recommendations

From the limited scope of the studies covered within this report, the Grassy Island CDF poses risks to the Service's trustee resources. These risks are long term in the absence of significant remedial actions to, or complete removal of the disposal facility. In addition, over time the facility will need to be maintained in its current state to keep the contaminated material from reentering the river.

Ultimately, the implementation of remedial actions to be proposed in the Remedial Action Plan for the river should cumulatively result in improved in water quality and the restoration of impaired beneficial uses. In light of this anticipated future situation, the Service should devise and implement a strategy to remediate the CDF structure so that all risks, both short and longterm, are minimized or eliminated.

Decommissioning the CDF with complete removal/treatment of its contents is one remedial strategy. The advantages are the complete elimination of risks to wildlife (and fish) and longterm maintenance costs. The disadvantage is the initial cost. At the other extreme is the no action alternative which should be construed as unacceptable in light of the present data. Intermediate actions may involve techniques to minimize exposure to wildlife (and fish) which could include installing a clean soil cap and grout wall, and other techniques employed at waste holding sites and landfills. The risk reduction from exposure is the obvious advantage. The disadvantages are the cost of construction and longterm maintenance, and the uncertainty of other routes of exposure, such as groundwater discharge and leachate to the river. Catastrophic failure of the facility is a possibility in a high energy environment such as this connecting channel.

We believe the only longterm solution to the CDF-derived risks is the complete decommissioning of the facility. The Service should give consideration to "leading by example" in the development of appropriate remediation technology that provides refuge remediation consistent with trustee responsibilities and technical assistance to the Detroit River remediation activities. The viability of removal and treatment of the contained wastes can be tested via a pilot demonstration project with other agencies employing a thermal gas-phase reduction process developed by Eco Logic, Inc. (Appendix 3). This process has recently been demonstrated on sediments contaminated with PCBs and PAHs from Hamilton, Ontario, and received favorable review by the Office of Technology Assessment, Congress of the United States (Appendix 4). A second demonstration project is scheduled for 1992 at Middle Ground Island, a PCB waste site in the Saginaw River in Michigan.

Normal waste incineration occurs in the presence of free oxygen and is somewhat controversial due to the formation of dioxin and furan compounds (Appendix 5). The Eco Logic process is oxygen-free but needs to be evaluated regarding heavy metals, primarily mercury, since these elements cannot be "destroyed" like organic compounds. It is grossly estimated that 1-2 million dollars would be required to appropriately characterize the chemistry of the destruction technology for a 30-day demonstration phase exercise, with concurrent analysis of appropriate fractions for PCB congeners, dioxins, furans, akyl-substituted PAHs and dibenzothiophenes.

In addition to the above, we offer the following recommendations for Service consideration:

1. Sediments/soils within the CDF should be resampled for additional H-4-II E bioassay analysis, employing fractionated extracts to better characterize the demonstrated toxic potency values of unfractionated extracts,

2. The facility should be posted prohibiting the hunting of waterfowl and upland game birds, due to the bioaccumulation of PCBs,

3. The facility should be decommissioned to eliminate the risks to trustee resources and allow for more management flexibility in the future,

4. Because of the nature of the site and its contamination by PCBs, PAHs and mercury, the Service should not seek disposal of this refuge property. It is unlikely that any pollution liability would be willingly accepted by another owner,

5 The Service should begin to conduct discussions with the Corps of Engineers, Detroit District on the use of the Defense Department's Defense Environmental Restoration Program to fund additional studies (including implementation of the Refuge monitoring program in the CDF and surrounding river refuge areas), demonstration and decommissioning activities consistent with Service needs. The Service also should enter into discussions with the USEPA, the State of Michigan and the Corps of Engineers on using the Grassy Island CDF as a model restoration site for the Detroit River specifically, and other areas generally. Other agency programs, such as the USEPA Geographic Enforcement Initiative in Southeast Michigan (Detroit River area) and the Remedial Action Plan process under the auspices of the Great Lakes Water Quality Agreement between Canada and the United States, would benefit from the participation of the Service as an active partner given the Service's real property and trustee resource issues in this ecosystem, and

6. An action plan for the Service (Divisions of Refuges and Wildlife, Research, and Fish and Wildlife Enhancement) might be considered for the longterm funding and implementation goals associated with the maintenance of the necessary Service presence and commitment to this refuge specifically, and the Detroit River generally.

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Table 1. Dry Weight Concentrations of Organic Compounds (ug/g) and Dioxin Equivalents (pg/g) in Aquatic Sediments and Terrestrial Soils within the Grassy Island CDF.

	Sediment		Soil[1]	
	North Cell	South Cell	Site A	Site B
Total PCBs[2]	2.0	2.0	0.96	0.96
p,p'-DDE	0.18	ND[5]	0.03	0.02
p,p'-DDD	0.18	ND	ND	ND
Chlordane	0.12	ND	ND	ND
Total Aromatics[3]	10.5	5.29	47.0	30.5
Total Aliphatics[4]	123.	17.9	-	-
TCDD-EQ	16591	1357	-	-

Beyer and Stafford, in press.
Guideline for open water disposal of dredged material for Total PCBs is 0.05 ug/g, dry weight, as established by:
- (a) International Joint Commission, Water Quality Board,
- (b) Ontario Ministry of the Environment, and
- (c) Wisconsin Department of Natural Resources, Technical Subcommittee on Determination of Dredge Material Suitability.

Summation of 14 Polynuclear Aromatic Hydrocarbon compounds.
Summation of 13 Aliphatic Hydrocarbon compounds.
Not detected, <0.01 ug/g, dry weight, for all indicated compounds.

Table 2. Dry Weight Concentrations of Heavy Metals (ug/g) in Aquatic Sediments and Terrestrial Soils within the Grassy Island CDF.

	Sediment		Soil[1]		
	N.Cell	S.Cell	Site A	Site B	Criteria[2]
Ba	430	444	220	190	20 (b)
Cd	13.7	14.3	11	10	1.0 (c,d)
Cr	295	282	210	140	25 (b,c)
Cu	278	260	300	210	25 (b,c)
Fe	46000	55400	49000	53000	10000 (c)
Hg	0.779	0.916	0.54	0.50	0.1 (d)
Mn	875	1180	770	980	300 (b)
Ni	85.3	84.4	64	56	20 (b)
Pb	486	480	410	330	40 (b)
Zn	1340	1510	1000	780	90 (b)

Beyer and Stafford, in press.
The most restrictive of the following 4 guidelines:

(a) International Joint Commission, Water Quality Board, Guidelines for Open Water Disposal of Dredged Material.

(b) 1977 U.S. Environmental Protection Agency, Guidelines for Open Water Disposal of Dredged Sediments.

(c) Ontario Ministry of the Environment, Guidelines for Open Water Disposal of Dredged Sediments.

(d) 1985 Wisconsin Department of Natural Resources, Report of the Technical Subcommittee on Determination of Dredge Material Suitability for In-Water Disposal.

Table 3. Wet Weight and Lipid Weight Concentrations of Organic Compounds (ug/g) in Skinless Breast Muscles from Waterfowl and Woodcock Collected within the Grassy Island CDF.

		Total PCBs		Total DDT		Total Aliphatics
		Wet Weight	Lipid Weight	Wet Weight	Lipid Weight	Wet Weight
North Cell						
C. Goose	Ad.M	ND[1]	ND[2]	0.02	1.2	0.28
	Ad.F	ND	ND	ND[3]	ND[4]	0.28
Mallard	Ad.M	0.89	53.[5]	0.02	1.2	0.41
	Ad.F	ND	ND	0.01	0.41	0.33
	Ad.F	ND	ND	0.02	1.6	0.23
Gadwall	Ad.M	ND	ND	ND	ND	0.42
South Cell						
B.W. Teal	Ad.M	0.94	44.[5]	0.13	6.0[6]	0.96
	Ad.F	0.54	93.[5]	0.04	6.9[6]	0.34
Woodcock[7]		1.1	31.[5]	0.10	2.8	0.36

[1] Total PCBs not detected, <0.05 ug/g, wet weight.
[2] Total PCBs not detected, ,<3.50 ug/g (mean), lipid weight.
[3] Total DDT not detected, <0.01 ug/g, wet weight.
Total DDT not detected, <0.86 ug/g (mean), lipid weight.
[5] Exceeds USFDA Tolerance Level for Total PCBs in poultry for interstate commerce, >3.0 ug/g, lipid weight.
[6] Exceeds USFDA Tolerance Level for Total DDT in poultry for interstate commerce, >5.0 ug/g, lipid weight.
Residues in wings were 3.5 ug/g Total PCBs, 0.54 ug/g Total DDT, and 0.81 ug/g Total Aliphatic Hydrocarbons, wet weight.

Table 4. Wet Weight and Lipid Weight Concentrations of Organic Compounds (ug/g) in Livers from Waterfowl and Woodcock Collected within the Grassy Island CDF.

		Total PCBs		Total DDT		Total Aliphatics
		Wet Weight	Lipid Weight	Wet Weight	Lipid Weight	Wet Weight
North Cell						
C. Goose	Ad.M[1]	ND[3]	ND[4]	ND[5]	ND[6]	0.28
	Ad.F[1]	ND	ND	ND	ND	0.14
	Juv.[1]	ND	ND	ND	ND	0.11
	Juv.[1]	ND	ND	ND	ND	0.09
	Juv.[1]	ND	ND	ND	ND	0.27
Mallard	Ad.M	1.0	31.[7]	0.06	1.9	0.56
	Ad.F	ND	ND	ND	ND	0.29
	Ad.F[2]	0.87	21.[7]	0.07	1.7	0.32
	Juv.[2]	0.39	7.2[7]	0.07	1.3	0.44
	Juv.[2]	2.5	57.[7]	0.08	1.8	0.39
	Juv.[2]	1.3	33.[7]	0.06	1.5	0.32
Gadwall	Ad.M	ND	ND	0.02	0.73	0.38
South Cell						
B.W. Teal	Ad.M	0.87	23.[7]	0.17	4.4	0.85
	Ad.F	2.4	46.[7]	0.56	11.[8]	1.14
Woodcock[9]		0.64	-	0.21	-	0.82

[1,2] Birds from the same family unit.

[3] Total PCBs not detected, <0.05 ug/g, wet weight.

Total PCBs not detected, <2.39 ug/g (mean), lipid weight.

[5] Total DDT not detected, <0.01 ug/g, wet weight.

[6] Total DDT not detected, <0.50 ug/g (mean), lipid weight.

[7] Exceeds USFDA Tolerance Level for Total PCBs in poultry for interstate commerce, >3.0 ug/g, lipid weight.

[8] Exceeds USFDA Tolerance Level for Total DDT in poultry for interstate commerce, >5.0 ug/g, lipid weight.

Residues in wings were 3.5 ug/g Total PCBs, 0.54 ug/g Total DDT, and 0.81 ug/g Total Aliphatic Hydrocarbons, wet weight.

Table 5. Wet Weight Concentrations of Heavy Metals (ug/g) in Skinless Breast Muscles from Waterfowl Collected within the Grassy Island CDF.

		Cr	Cu	Hg
North Cell				
Canada Goose	Ad.M[1]	0.81	9.9	0.02
	Ad.F[1]	0.50	5.2	0.03
Mallard	Ad.M	0.51	4.2	0.07
	Ad.F	0.89	5.5	0.05
	Ad.F	0.78	6.5	0.22
Gadwall	Ad.M	0.94	6.1	0.15
South Cell				
Blue-Winged Teal	Ad.M	0.48	4.6	0.67
	Ad.F	0.43	4.2	0.51

Mated pair.

Table 6. Wet Weight Concentrations of Heavy Metals (ug/g) in Livers from Waterfowl Collected within the Grassy Island CDF.

		Cd	Cr	Cu	Hg	Pb
North Cell						
Canada Goose	Ad.M[1]	0.66	0.54	8.2	0.08	1.32
	Ad.F[1]	0.66	0.43	1.9	0.10	1.50
	Juv.[1]	0.85	1.05	8.4	0.04	5.19
	Juv.[1]	ND[3]	0.53	10.7	0.06	ND[4]
	Juv.[1]	ND	0.42	11.0	0.07	ND
Mallard	Ad.M	1.43	0.71	53.1	0.25	2.45
	Ad.F	0.38	0.53	14.3	0.25	ND
	Ad.F[2]	0.38	0.50	28.8	0.43	ND
	Juv.[2]	ND	0.65	33.8	0.35	ND
	Juv.[2]	ND	0.54	19.4	0.27	ND
	Juv.[2]	ND	0.52	19.2	0.36	ND
Gadwall	Ad.M	2.89	0.65	44.7	0.27	1.60
South Cell						
Blue-Winged Teal	Ad.M	0.73	0.67	14.6	2.13	1.10
	Ad.F	0.32	0.68	11.1	0.90	ND

[1,2] Birds from the same family unit.
[3] Cd Not detected, <0.058 ug/g, wet weight.
Pb Not detected, <0.42 ug/g, wet weight.

Table 7. Estimated Lipid Weight Concentrations of Organic Compounds (ug/g) in Woodcock Wings from Grassy Island CDF, Compared to Previous Michigan Surveys.

	Grassy Island[1]	Michigan Surveys[2]		
	1988	1970-71[3]	1971-72[4]	1975[5]
Total PCBs	24.31	3.75-4.70	1.02-2.21	1.19-2.06
p,p'-DDE	3.75	1.89-13.59	2.28-6.96	1.74-4.50
Dieldrin	0.35	0.12-0.44	0.07-0.11	0.04-0.09
t-Nonachlor	0.63	-	-	0.04-0.09
Mirex	5.69	0.49-5.72	0.59-5.01	0.49-2.19
Heptachlor Epoxide	0.14	-	ND[6]	0.08-0.17
Aldrin	3.68	-	-	-

Assumes lipid content in woodcock wings is similar to mallard wings (14.4%) in Michigan (Prouty and Bunck 1986).
Data expressed as a range of concentrations for 5 composite samples of 25 wings each.
McLane *et al.* 1973.
McLane *et al.* 1978.
McLane *et al.* 1984.
Not detected, <0.05 ug/g, lipid weight.

Table 8. Fresh Wet Weight Concentrations of Organic Compounds (ug/g) and Dioxin Equivalents (pg/g) in Common Tern and Forster's Tern Egg Composites from the Detroit River, Lake St.Clair and the Saginaw River and Bay.

	Common Tern			Forster's Tern
	Saginaw River	Saginaw Bay	Pointe Mouillee	Lake St.Clair
Total PCBs	9.1[2]	7.3[2]	11.[2]	6.6[2]
p,p'-DDE	0.84	0.75	0.86	0.90
Total DDT	0.89	0.85	1.0	0.97
Dieldrin	0.07	0.06	0.07	0.08
Heptachlor Epoxide	0.06	ND[3]	0.06	0.04
t-Nonachlor	0.04	0.04	0.03	0.13
Total Aliphatics[1]	0.27	0.55	0.67	0.71
TCDD-EQ	-	180.4	146.9	85.3

Summation of 13 Aliphatic Hydrocarbon compounds.

[2] Exceeds USFDA Tolerance Level for Total PCBs in eggs for interstate commerce >0.3 ug/g, wet weight.

[3] Not detected, <0.01 ug/g, fresh wet weight.

Table 9. Fresh Wet Weight Concentrations of Heavy Metals (ug/g) in Common Tern and Forster's Tern Egg Composites from the Detroit River, Lake St.Clair and the Saginaw River and Bay.

	Common Tern			Forster's Tern
	Saginaw River	Saginaw Bay	Pointe Mouillee	Lake St.Clair
Ba	0.07	0.16	0.27	0.15
Cr	0.27	0.29	0.50	0.39
Cu	0.69	0.70	0.77	0.81
Fe	27.	28.	59.	28.
Hg	0.83	0.84	1.27	1.69
Mn	0.39	0.48	1.21	0.35
Zn	13.	14.	17.	15.

Note: Not detected were Cd (<0.04 ug/g, fww), Pb (<0.30 ug/g, fww) and Ni (<0. 7 ug/g, fww).